

Ionic liquids having $[\text{N}(\text{CF}_3)_2]^-$ anions

The present invention relates to salts comprising bis(trifluoromethyl)imide anions and saturated, partially or fully unsaturated, heterocyclic cations, to a process for the preparation thereof, and to the use thereof as ionic liquids.

Ionic liquids or liquid salts are ionic species which consist of an organic cation and a generally inorganic anion. They do not contain any neutral molecules and have melting points of below 373 K. A multiplicity of compounds which are used as ionic liquids are known in the prior art. In particular, they are also the subject-matter of a series of patents and patent applications.

Thus, solvent-free ionic liquids were disclosed for the first time by Hurley and Wier in a series of US patents (US 2,446,331, US 2,446,339 and US 2,446,350). These "salts which are molten at room temperature" comprised AlCl_3 and a multiplicity of n-alkylpyridinium halides.

US 5,827,602 describes hydrophobic ionic liquids having a wide electrochemical window for use as electrolytes in batteries. These salts have certain 5- or 6-membered heterocyclic cations and polyatomic anions having a van der Waals radius of greater than 100 \AA^3 , for example halogenated alkylsulfonimides, mono- or diperfluorosulfonates, fluorinated alkylfluorophosphates.

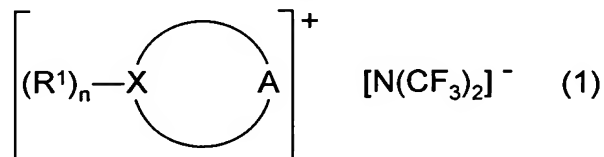
In addition, some review articles on this topic have been published in recent years (R. Sheldon "Catalytic reactions in ionic liquids", *Chem. Commun.*, 2001, 2399-2407; M.J. Earle, K.R. Seddon "Ionic liquids. Green solvent for the future", *Pure Appl. Chem.*, 72 (2000), 1391-1398; P. Wasserscheid, W. Keim "Ionische Flüssigkeiten – neue Lösungen für die Übergangsmetallkatalyse" [Ionic Liquids – Novel Solutions for Transition-Metal Catalysis], *Angew. Chem.*, 112 (2000), 3926-3945; T. Welton "Room temperature ionic liquids. Solvents for synthesis and catalysis", *Chem. Rev.*, 92 (1999), 2071-2083; R. Hagiwara, Ya. Ito "Room temperature ionic liquids of alkylimidazolium cations and fluoroanions", *Journal of Fluorine Chem.*, 105 (2000), 221-227).

EP 1 081 129 discloses stable $\text{N}(\text{CF}_3)_2^-$ salts having tetraalkylammonium and comparable cations. Neither heterocyclic cations nor use of the disclosed compounds as ionic liquids are described.

- 5 The properties of ionic liquids, for example melting point, thermal and electro-chemical stability, viscosity, are greatly influenced by the nature of the anion. By contrast, the polarity and hydrophilicity or lipophilicity can be varied through a suitable choice of the cation/anion pair. There is therefore a demand for novel ionic liquids having varied properties which facilitate additional possibilities regarding
10 their use.

The object of the present invention is to provide novel stable compounds having valuable properties which can be used as ionic liquids, and a process for the
15 preparation thereof.

This object is achieved by the provision of salts of the general formula (1)



which have a bis(trifluoromethyl)imide anion and a saturated, partially or fully unsaturated, heterocyclic cation.

20 In this formula:

X denotes N, P, O or S

- 25 n denotes an integer selected from 0, 1 or 2 in such a way that X is saturated in accordance with its valency increased by 1,

A denotes a saturated, partially or fully unsaturated 3- to 8-membered hydrocarbon chain,

- 30 in which all carbon atoms apart from one may be replaced by identical or different heteroatoms, selected from N, P, O and S, where the carbon atoms of the hydrocarbon chain and the heteroatoms present therein are saturated by substituents R^2 in accordance with their valency,

R^1, R^2 denote -H, with the proviso that there is no bond to the positively charged heteroatom,
straight-chain or branched alkyl having 1-20 carbon atoms
5 straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds
straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds
saturated, partially or fully unsaturated cycloalkyl having 3-7 carbon
10 atoms
halogen, in particular fluorine or chlorine, with the proviso that, for X = N, O, S, there is no halogen-heteroatom bond,
-NO₂, with the proviso that there is no bond to the positively charged heteroatom,
15 -CN, with the proviso that there is no bond to the positively charged heteroatom,

where the R^2 and/or R^1 in different and/or identical position of the heterocyclic ring are in each case identical or different,

where the R^2 and/or R^1 may be connected to one another in pairs by a single or double bond,

where one or more R^2 and/or R^1 may be partially or fully substituted by halogens, in particular -F and/or -Cl, or partially by -CN or -NO₂, with the proviso that not all R^2 and R^1 are fully halogenated,

and where one or two carbon atoms of the R^1 and/or R^2 may be replaced by heteroatoms and/or atomic groups selected from the group
30 -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -N=, -P=, -NH-, -PH-, -NR'- and -PR'- where R' = non-, partially or perfluorinated C₁- to C₆-alkyl or -C₆F₅, where the α -position of the R^1 is not replaced for X = O, S.

35 For the purposes of the present invention, the valency of the atom is taken to mean the number of bonds which emanate from a neutral atom or the number of electron pairs that a neutral atom shares with other atoms in a molecule and which

are represented as valence dashes in the simplified representation of the electron formulae. In accordance with the invention, nitrogen and phosphorus atoms therefore have a valency of 3, oxygen and sulfur atoms a valency of 2 and carbon atoms a valency of 4. Phosphorus atoms may, if they are neutral atoms of the cation, also have a valency of 5.

For the purposes of the present invention, fully unsaturated compounds or substituents are also taken to mean aromatic compounds or aromatic substituents.

- 10 The compounds according to the invention are salts which have an $\text{N}(\text{CF}_3)_2^-$ anion and, as cation, a heterocyclic 4- to 9-membered ring, which is saturated or unsaturated. Suitable heteroatoms here are N, P, O or S. Besides the heteroatom carrying the positive charge, the heterocyclic ring may also contain further, identical or different heteroatoms selected from the group N, P, O and S; however, the ring
- 15 contains at least one carbon atom.

Suitable cations according to the invention are heterocyclic compounds which are stable, in particular which can be isolated.

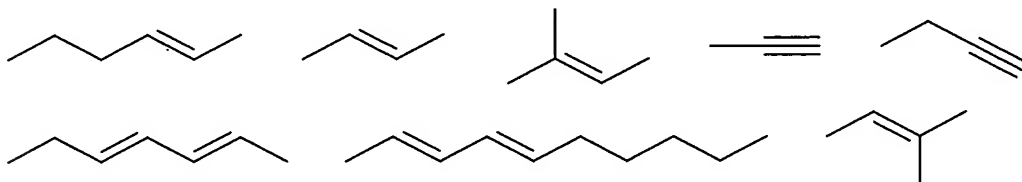
- 20 All atoms of the heterocyclic ring each carry so many identical or different substituents R^1 or R^2 that they are saturated in accordance with their valency. In the case of the positively charged heteroatom, the number of substituents corresponds to the valency increased by 1.
- 25 Some examples are given below which are intended to document the number of substituents per ring atom in accordance with the invention: monounsaturated or aromatic, i.e. sp^2 -hybridised, carbon atoms have one substituent, while saturated sp^3 -hybridised carbon atoms have two substituents. An oxygen or sulfur atom carrying a positive charge which is bonded into the cyclic ring by means of a
- 30 double bond has no substituents, just like an oxygen or sulfur atom with no positive charge which is singly bonded into the cyclic ring and a nitrogen or phosphorus atom with no positive charge which is bonded into the cyclic ring by means of a double bond. Oxygen or sulfur atoms having a positive charge which are singly bonded into the cyclic ring and nitrogen or phosphorus atoms having a positive
- 35 charge which are bonded into the cyclic ring by means of a double bond and nitrogen or phosphorus atoms with no positive charge which are singly bonded into the cyclic ring carry one substituent.

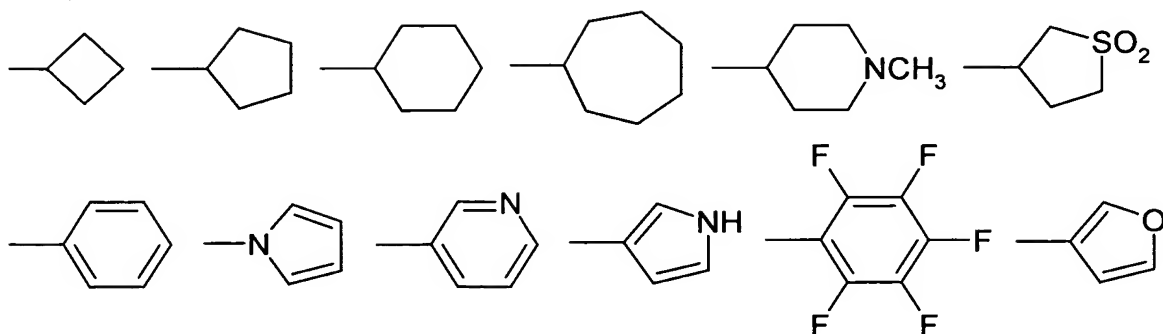
Besides hydrogen, suitable substituents R^1 , R^2 of the heterocyclic ring are, in accordance with the invention: C_1 - to C_{20} -, in particular C_1 - to C_{12} -alkyl groups, C_2 - to C_{20} -, in particular C_2 - to C_{12} -, alkenyl or alkynyl groups, saturated or unsaturated, i.e. also aromatic, C_3 - to C_7 -cycloalkyl groups, NO_2 , CN or halogens. For the halogens, however, a restriction is that they only occur as substituents on carbon atoms or on phosphorus atoms of the heterocyclic ring, but not on the heteroatoms N, O, S. H, NO_2 and CN do not occur as substituents of the positively charged heteroatom.

The substituents R^1 , R^2 may also be connected in pairs in such a way that bi- or polycyclic cations arise. The substituents may be partially or fully substituted by halogen atoms, in particular by F and/or Cl, or partially by CN or NO_2 and contain one or two heteroatoms or atomic groups selected from the group O, C(O), C(O)O, S, S(O), SO_2 , SO_2O , N, P, NH, PH, NR' , PR' . In the case of full halogenation, however, not all substituents R^1 and R^2 present may be fully halogenated, i.e. at least one R^1 and/or R^2 is not perhalogenated.

Without restricting generality, examples of substituents according to the invention of the heterocyclic cation are:

-F, -Cl, -Br, -I, -CH₃, -C₂H₅, -C₃H₇, -CH(CH₃)₂, -C₄H₉, -C(CH₃)₃, -C₅H₁₁, -C₆H₁₃, -C₆H₁₃, -C₇H₁₅, -C₈H₁₇, -C₉H₁₉, -C₁₀H₂₁, -C₁₂H₂₅, -C₂₀H₄₁, -OCH₃, -OCH(CH₃)₂, -CH₂OCH₃, -C₂H₄OCH(CH₃)₂, -SCH₃, -SCH(CH₃)₂, -C₂H₄SC₂H₅, -C₂H₄SCH(CH₃)₂, -S(O)CH₃, -SO₂CH₃, -SO₂C₂H₅, -SO₂C₃H₇, -SO₂CH(CH₃)₂, -CH₂SO₂CH₃, -OSO₂CH₃, -OSO₂CF₃, -CH₂N(H)C₂H₅, -C₂H₄N(H)C₂H₅, -CH₂N(CH₃)CH₃, -C₂H₄N(CH₃)CH₃, -N(CH₃)₂, -N(CH₃)C₃H₅, -N(CH₃)CF₃, O-C₄H₈-O-C₄H₉, -S-C₂H₄-N(C₄H₉)₂, -OCF₃, -S(O)CF₃, -SO₂CF₃, -CF₃, -C₂F₅, -C₃F₇, -C₄F₉, -C(CF₃)₃, -CF₂SO₂CF₃, -C₂F₄N(C₂F₅)C₂F₅, -CF=CF₂, -C(CF₃)=CFCF₃, -CF₂CF=CFCF₃, -CF=CFN(CF₃)CF₃, -CFH₂, -CHF₂, -CH₂CF₃, -C₂F₂H₃, -C₃FH₆, -CH₂C₃F₇, -C(CFH₂)₃, -CHO, -C(O)OH, -CH₂C(O)OH, -CH₂C(O)CH₃, -CH₂C(O)C₂H₅, -CH₂C(O)OCH₃, CH₂C(O)OC₂H₅, -C(O)CH₃, -C(O)OCH₃,





5 According to model calculations, the $[N(CF_3)_2]^-$ anion has a van der Waals radius of 90.90 \AA^3 and is thus relatively small compared with the ionic liquid anions known from the prior art.

10 The salts according to the invention are not hydrophobic, i.e. they are at least to a certain extent miscible with water.

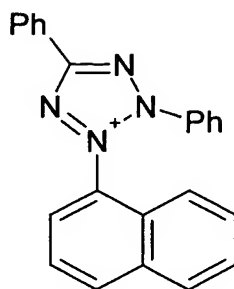
In addition, the salts according to the invention are advantageously very highly soluble in organic solvents.

15 Compared with known liquid salts, the salts according to the invention surprisingly have low viscosity.

Advantageously, the salts according to the invention are stable. They can be isolated and stored at room temperature.

20 Furthermore, the salts according to the invention are relatively simple to prepare, while, in particular, the $[N(SO_2CF_3)_2]^-$ anion known from the prior art is only accessible with difficulty and in particular is very expensive.

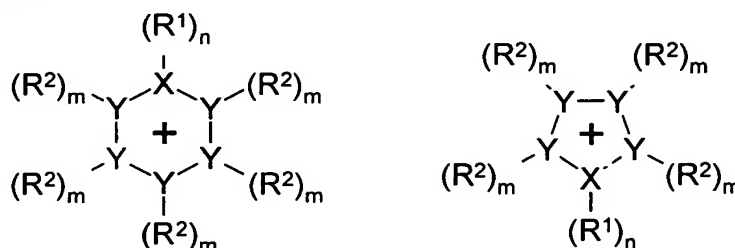
25 In salts which are preferred in accordance with the invention, the cation has a heterocyclic, saturated or unsaturated five-, six- or seven-membered ring. An example of a five-membered ring according to the invention having only one carbon atom is the tetrazolium cation, for example in



In a further preferred variant of the salts according to the invention, the heterocyclic ring of the cation contains a total of at most 3 heteroatoms selected from N, P, O or S. In the case of a plurality of heteroatoms, it is very particularly preferred for only a maximum of 2 heteroatoms to be arranged directly adjacent.

Besides hydrogen atoms, preferred substituents for the heterocyclic ring are halogens, in particular fluorine, so long as these are not bonded to a heteroatom with the exception of phosphorus, straight-chain or branched C₁- to C₆-alkyl groups, in particular -CH₃, -C₂H₅, -*n*-C₃H₇, -CH(CH₃)₂, -*n*-C₄H₉, -*n*-C₆H₁₃ and straight-chain or branched, partially or perfluorinated C₁- to C₆-alkyl groups, in particular -CF₃, -C₂F₅, -C₄F₉.

A preferred embodiment of the invention are salts in which the saturated, partially or fully unsaturated heterocyclic cation is a five- or six-membered ring having the following structure:



where X is selected from the group N, P, O and S and

Y is in each case, independently of one another, selected from the group C, N, P, O and S,

where at least one Y is a carbon atom, while the remaining three or four Y can be carbon or heteroatoms.

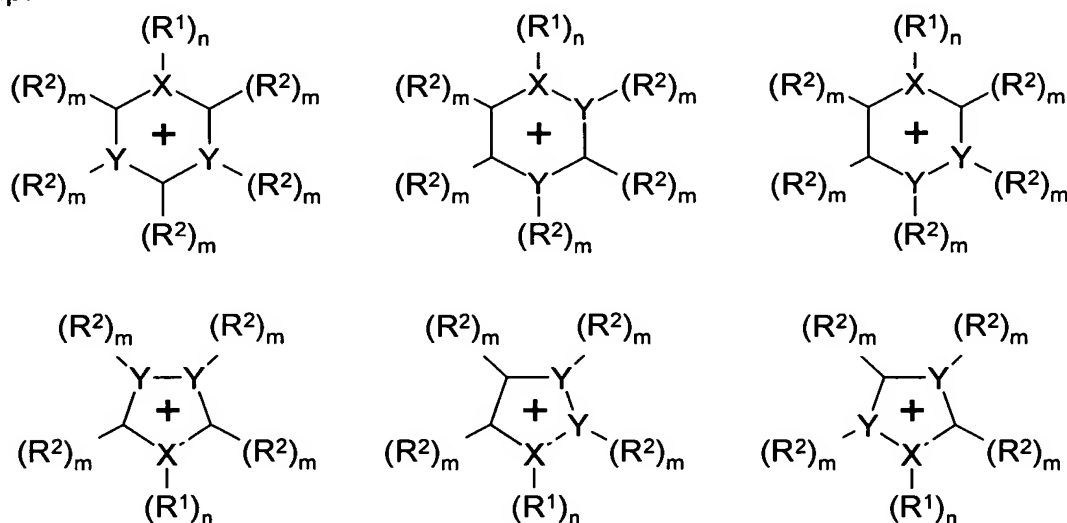
The number n of substituents R¹ on the positively charged heteroatom X corresponds to the valency increased by 1, i.e. unsaturated oxygen or sulfur atoms have no substituents, saturated oxygen and sulfur atoms, like unsaturated nitrogen

and phosphorus atoms, have one substituent R^1 and saturated nitrogen and phosphorus atoms have two substituents R^1 .

The remaining atoms (Y) of the heterocyclic ring each have so many (m) identical or different substituents R^2 that they are saturated in accordance with their valency, i.e. saturated oxygen and sulfur atoms, like unsaturated nitrogen and phosphorus atoms, have no substituents, saturated nitrogen and phosphorus atoms as well as unsaturated, sp^2 -hybridised carbon atoms have one substituent R^2 and saturated, sp^3 -hybridised carbon atoms have two substituents R^2 .

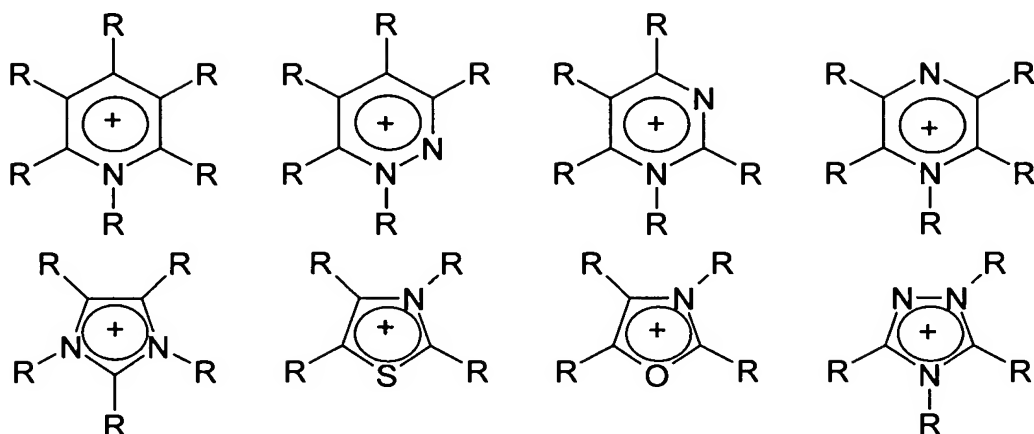
The substituents R^1 and R^2 are defined as in the general formula (1).

In this embodiment, particular preference is given to the variants in which the heteroatoms of the saturated or unsaturated five- or six-membered ring of the cation are distributed in such a way that the cation is selected from the following group:



where X selected from the group N, P, O and S and Y in each case, independently of one another, selected from the group C, N, P, O and S. The number n, m of substituents R^1 , R^2 on the positively charged heteroatom X or the remaining atoms of the heterocyclic ring are defined in accordance with the general formulae for the five- or six-membered ring cations. The substituents R^1 and R^2 are defined as in the general formula (1).

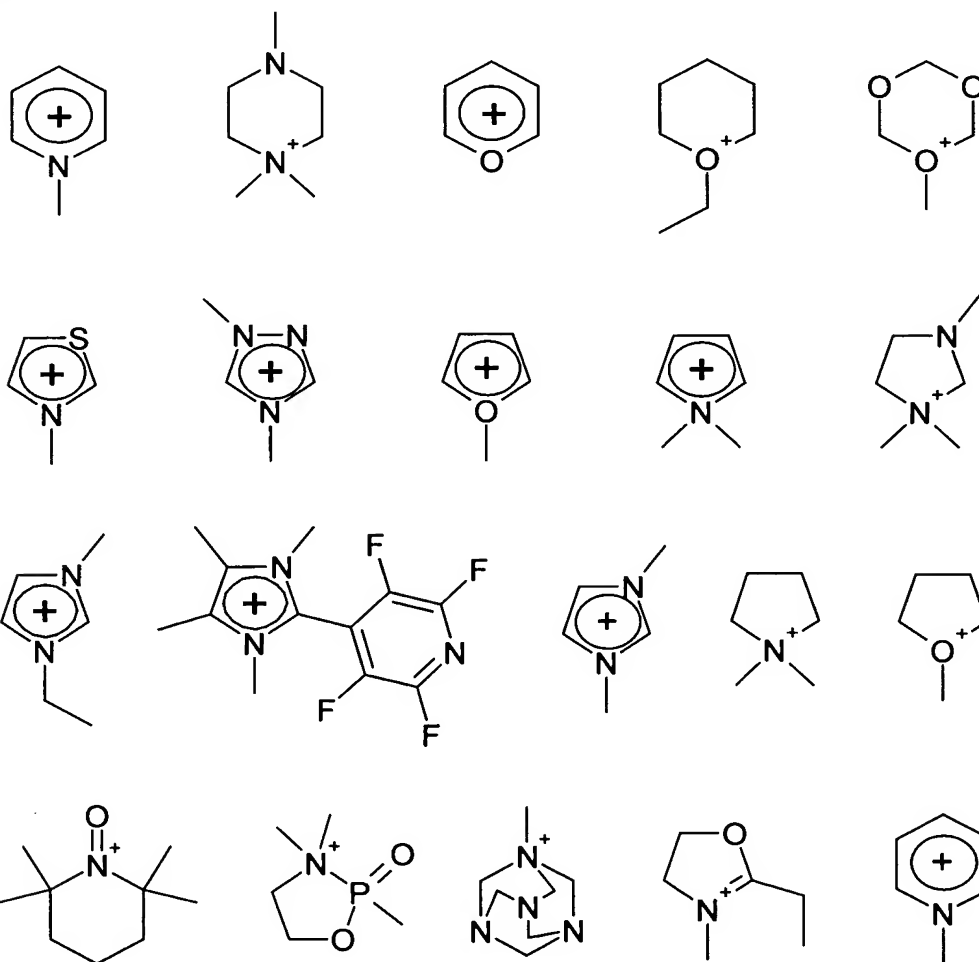
Without restricting generality, examples of such cations according to the invention having a five- or six-membered ring are:



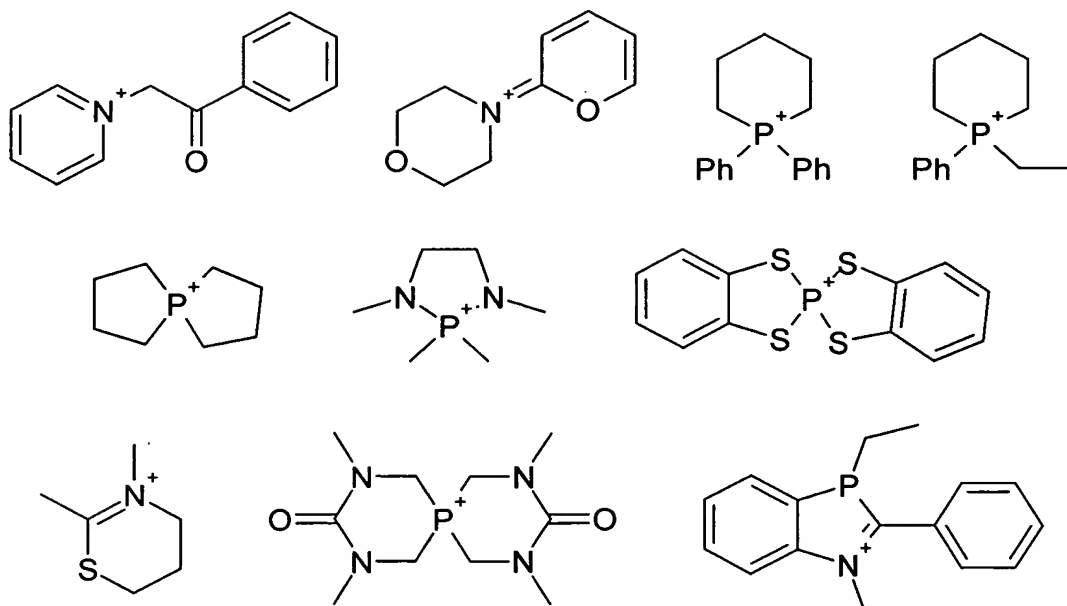
where the substituents R are defined, independently of one another, like R¹ and R² in the general formula (1),

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and also



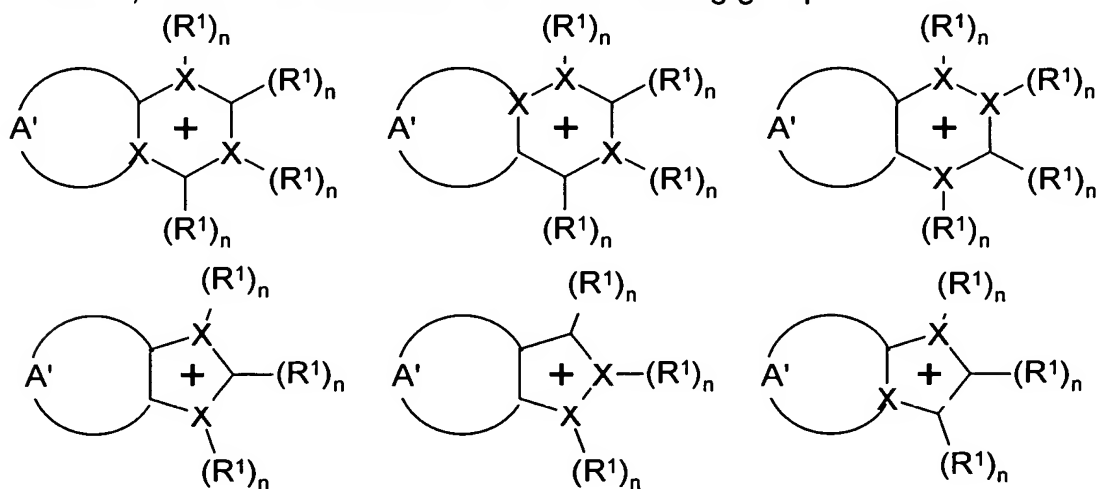
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In a further preferred variant, salts according to the invention have a saturated, partially or fully unsaturated, heterocyclic cation which contains a fused ring, i.e. a cation in which two adjacent substituents of the heterocyclic ring are connected to one another, and which is selected from the following group:

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where X in each case, independently of one another, selected from the group N, P, O, S and C, where at least one X = N, P, O or S.

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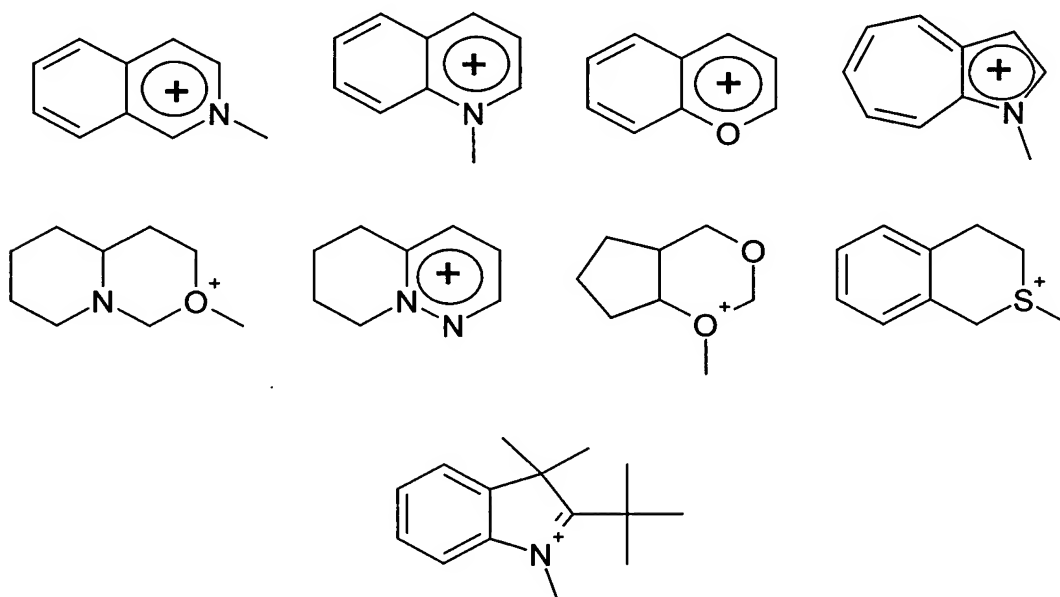
The atoms of the heterocyclic ring each have so many (n) identical or different substituents R^1 that they are saturated in accordance with their valency, where n is increased by 1 for the heteroatom X carrying the positive charge.

A' has the meaning of a saturated, partially or fully unsaturated 2- to 7-membered hydrocarbon chain, where the carbon atoms of the hydrocarbon chain are saturated by substituents R^2 in accordance with their valency.

- 5 The substituents R^1 and R^2 are defined as in the general formula (1), but where the substituents R^1 in the α -position to the positively charged heteroatom do not have a methylene group directly adjacent to the heterocyclic ring.

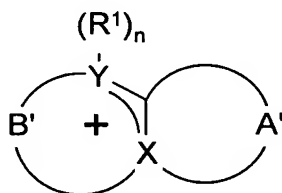
Without restricting generality, examples of such cations according to the invention

10 are :



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Preference is furthermore given to salts according to the invention in which the saturated, partially or fully unsaturated heterocyclic cation has the following structure:



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where X selected from the group N and P and Y selected from the group N, P, O and S.

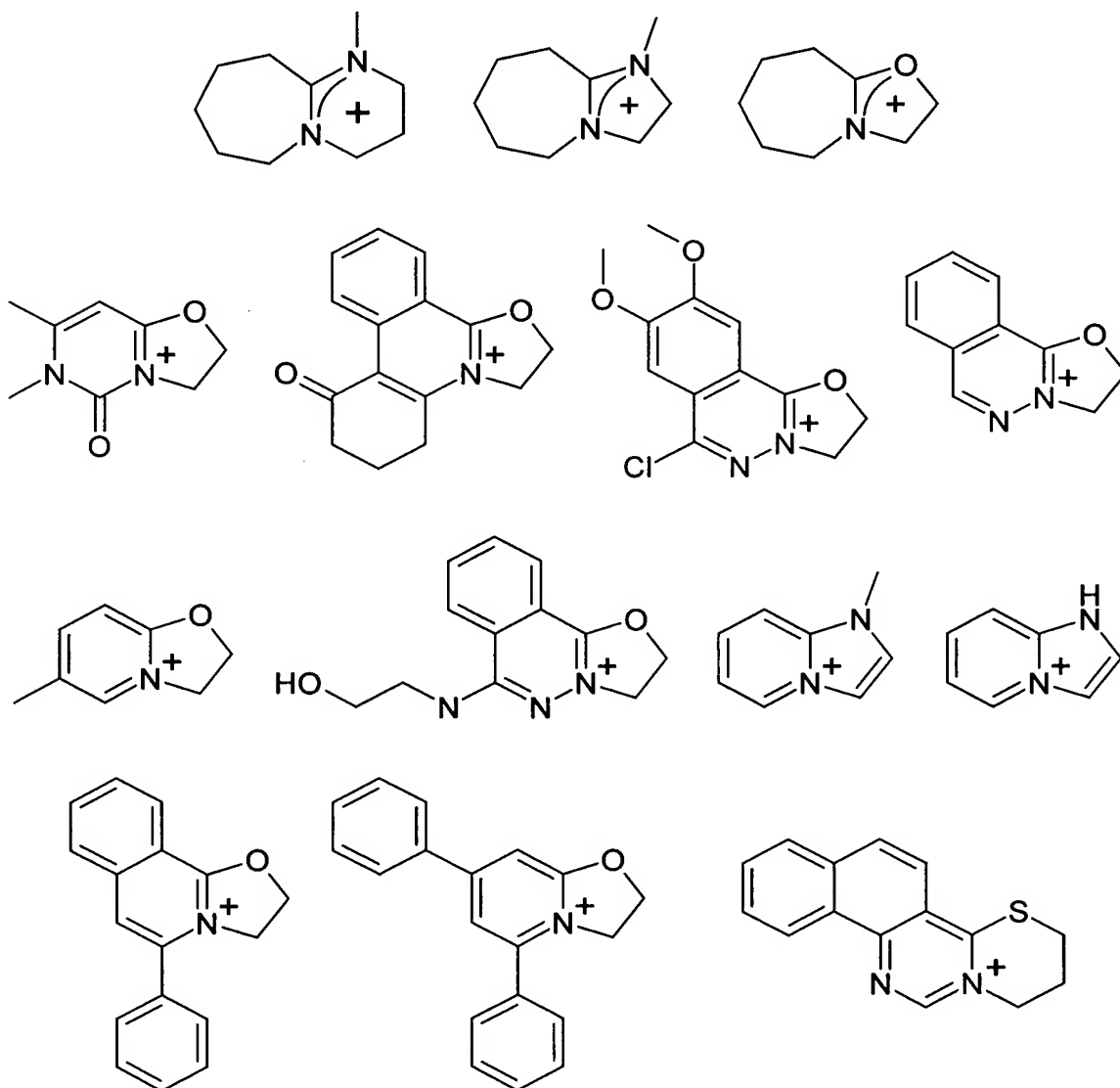
The number n of substituents R^1 on the heteroatom Y is 0 in the case of an oxygen or sulfur atom and is 1 in the case of a nitrogen or phosphorus atom.

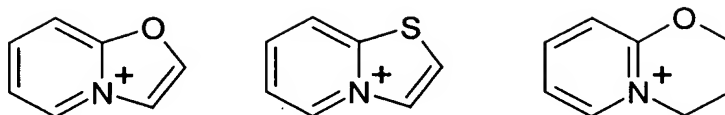
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A' has the meaning of a 2- to 7-membered, B' that of a 1- to 6-membered hydrocarbon chain, where the hydrocarbon chains are saturated, partially or fully unsaturated and in which all carbon atoms apart from one may be replaced by identical or different heteroatoms selected from N, P, O and S and where the carbon atoms of the hydrocarbon chains A' and B' are saturated by substituents R² in accordance with their valency.

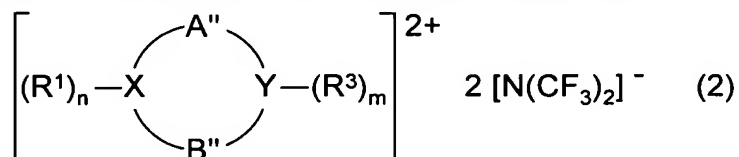
The substituents R¹ and R² are defined as in the general formula (1).

Without restricting generality, examples of such cations according to the invention are :





The present invention relates secondly to salts of the general formula (2)



which contain a bis(trifluoromethyl)imide anion and a saturated or unsaturated, heterocyclic di-cation, i.e. a heterocyclic 4- to 9-membered ring which is saturated or unsaturated and contains two positively charged heteroatoms.

In this formula:

X, Y each, independently of one another, denote N, P, O or S

n, m denote an integer selected from 0, 1 or 2 in such a way that X, Y are each saturated in accordance with their valency increased by 1,

A'', B'' denote saturated, partially or fully unsaturated 0- to 4-membered hydrocarbon chain,
in which the carbon atoms may be replaced by identical or different heteroatoms selected from N, P, O and S,
where at least one carbon atom is present in the chains A'' and B'' together and
where the carbon atoms of the hydrocarbon chains A'' and B'' and the heteroatoms present therein are saturated by substituents R² in accordance with their valency,

R¹, R², R³ denote -H, with the proviso that there is no bond to the positively charged heteroatom,

straight-chain or branched alkyl having 1-20 carbon atoms

straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds

straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds

saturated, partially or fully unsaturated cycloalkyl having 3-7 carbon atoms

5 halogen, in particular fluorine or chlorine, with the proviso that, for X = N, O, S, there is no halogen-heteroatom bond,

-NO₂, with the proviso that there is no bond to a positively charged heteroatom,

10 -CN, with the proviso that there is no bond to a positively charged heteroatom,

where the R¹, R² and/or R³ in different and/or identical position of the heterocyclic ring are in each case identical or different,

15 where the R¹, R² and/or R³ may be connected to one another in pairs by a single or double bond,

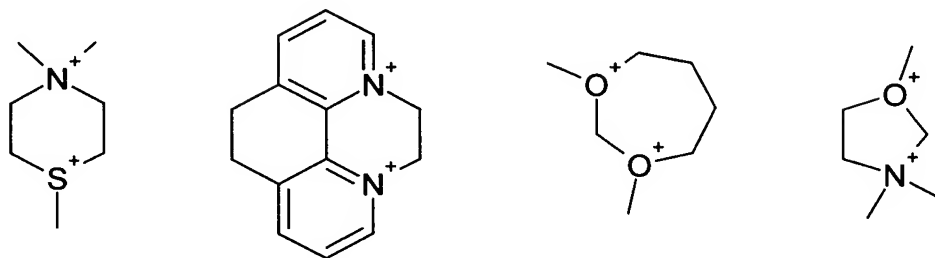
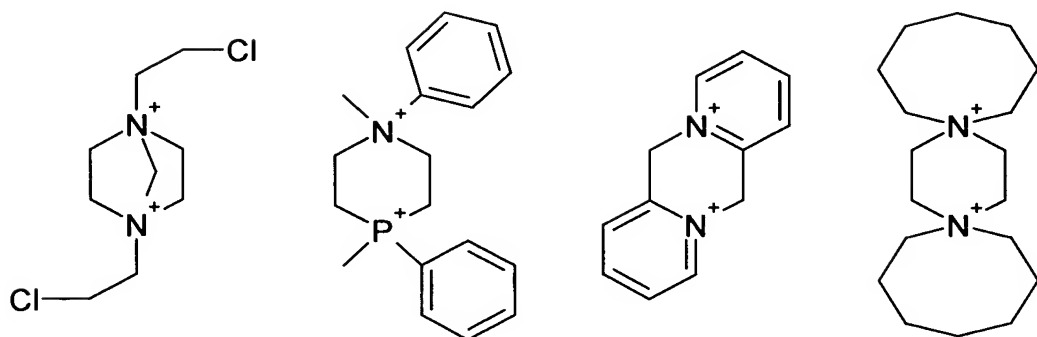
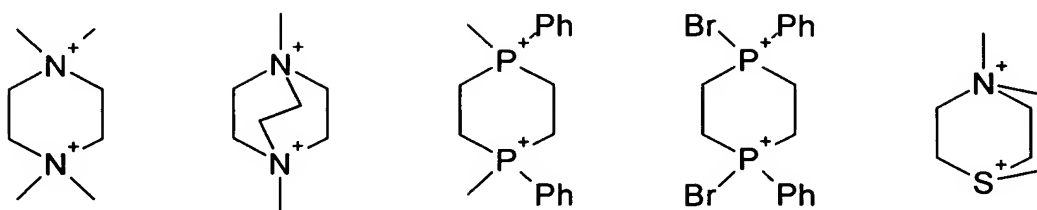
20 where one or more R¹, R² and/or R³ may be partially or fully substituted by halogens, in particular -F and/or -Cl, or partially by -CN or -NO₂, with the proviso that not all R¹, R² and R³ are fully halogenated,

25 and where one or two carbon atoms of the R¹, R² and/or R³ may be replaced by heteroatoms and/or atomic groups selected from the group -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -N=, -P=, -NH-, -PH-, -NR'- and -PR'- where R' = non-, partially or perfluorinated C₁- to C₆-alkyl or -C₆F₅, where the α-positions of the R¹ and of the R³ are not replaced for X = O, S or Y = O, S,

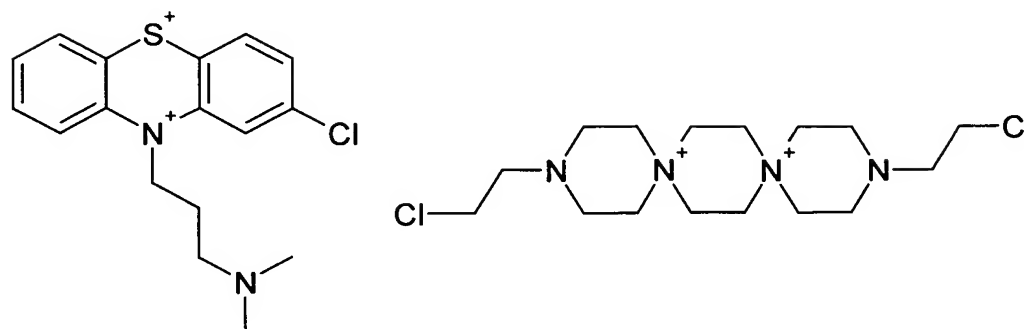
30 where the heterocyclic di-cation is a 4-, 5-, 6-, 7-, 8- or 9-membered ring.

In preferred salts, the di-cation has a heterocyclic, saturated or unsaturated five-, six- or seven-membered ring.

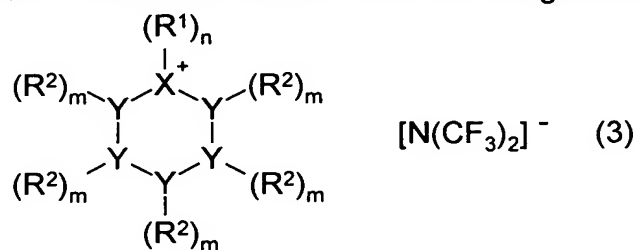
35 Without restricting generality, examples of such di-cations according to the invention are:



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The present invention furthermore relates to salts of the general formula (3)



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which contain a bis(trifluoromethyl)imide anion and a saturated partially or fully unsaturated, heterocyclic cation whose heterocyclic six-membered ring contains no carbon atoms.

5

In this formula:

X, Y each, independently of one another, denote N, P, O or S

10

n denotes an integer selected from 0, 1 or 2 in such a way that X is saturated in accordance with its valency increased by 1,

m denotes an integer selected from 0, 1 or 2 in such a way that Y is saturated in accordance with its valency,

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R¹, R² denote -H, with the proviso that there is no bond to the positively charged heteroatom,
straight-chain or branched alkyl having 1-20 carbon atoms
straight-chain or branched alkenyl having 2-20 carbon atoms and one or more double bonds
straight-chain or branched alkynyl having 2-20 carbon atoms and one or more triple bonds
saturated, partially or fully unsaturated cycloalkyl having 3-7 carbon atoms

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halogen, in particular fluorine or chlorine, with the proviso that, for X = N, O, S, there is no halogen-heteroatom bond,
-OR, with the proviso that the substituted heteroatom is not O or S,

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where the R² and/or R¹ in different and/or identical position of the heterocyclic ring are in each case identical or different,

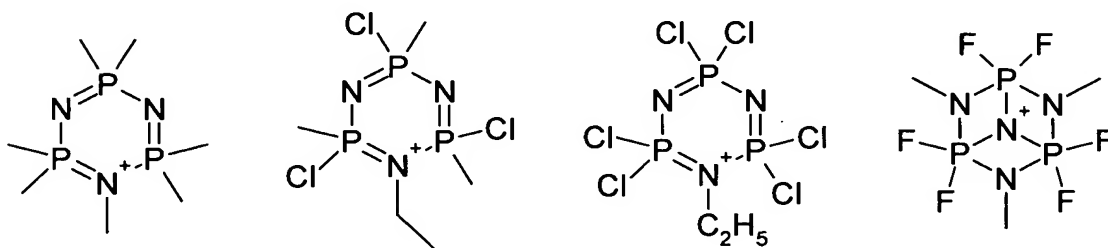
where the R² and/or R¹ may be connected to one another in pairs by a single or double bond,

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where one or more R² and/or R¹ may be partially or fully substituted by halogens, in particular -F and/or -Cl, or partially by -CN or -NO₂, with the proviso that not all R² and R¹ are fully halogenated,

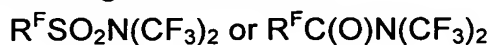
and where one or two carbon atoms of the R^1 and/or R^2 may be replaced by heteroatoms and/or atomic groups selected from the group
 -O-, -C(O)-, C(O)O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -N=, -P=, -NH-, -PH-,
 -NR'- and -PR'- where R' = non-, partially or perfluorinated C₁- to C₆-
 alkyl or -C₆F₅, where the α -position of the R^1 is not replaced for X = O,
 S.

Without restricting generality, examples of such cations according to the invention
 are :



It has been found that the compounds according to the invention can easily be
 synthesised under mild conditions. The salts according to the invention are iso-
 lated with high yields.

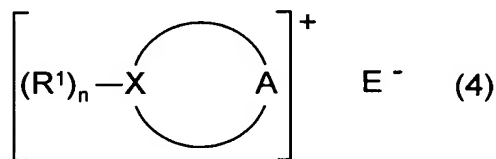
To this end, compounds of the general formula



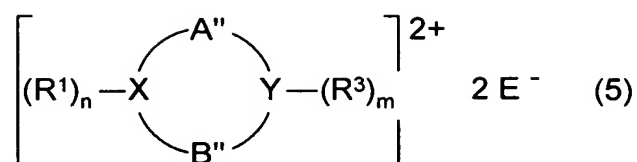
where $R^F = F$ or $C_p F_{2p+1}$, where $p = 1 - 8$,
 are reacted with an alkali metal fluoride of the general formula

DF, where D selected from the group of the alkali metals,

in a polar organic solvent, and subsequently or simultaneously a salt of the general
 formula (4)



or a salt of the general formula (5)



having a saturated, partially or fully unsaturated, heterocyclic 4- to 9-membered mono- or di-cation and an anion E^- selected from the group F^- , Cl^- , Br^- , I^- , BF_4^- , ClO_4^- , AsF_6^- , SbF_6^- , SbCl_6^- , PF_6^- , $\text{R}^{\text{F}}\text{SO}_3^-$, FSO_3^- , $(\text{R}^{\text{F}})_2\text{P}(\text{O})\text{O}^-$, $\text{R}^{\text{F}}\text{P}(\text{O})_2\text{O}^-$, RSO_3^- , ROSO_3^- , $\frac{1}{2}\text{SO}_3^{2-}$, CN^- , SCN^- , $\text{R}^{\text{F}}\text{C}(\text{O})\text{O}^-$, $\text{RC}(\text{O})\text{O}^-$, 2,4-dinitrophenolate and 2,4,6-trinitrophenolate, where R^{F} = perfluorinated C_1 to C_8 -alkyl group or per-fluorinated aryl group and $\text{R} = \text{C}_1$ to C_8 -alkyl group or aryl group, is added.

The heteroatoms X and Y, the parameters n and m, the hydrocarbon chains A, A'' and B'' and the substituents R^1 , R^2 and R^3 of the salts of the general formula (4) or (5) are defined here as those in the general formulae (1) and (2).

In the reaction, fluoroalkylated sulfonic acid bis(trifluoromethyl)amide is preferably used for the reaction with the alkali metal fluoride.

In a variant which is preferred in accordance with the invention, the process is carried out as a one-pot reaction, i.e. the intermediate from alkali metal fluoride and fluoroalkylated sulfonic acid bis(trifluoromethyl)amide or acylbis(trifluoromethyl)-amide is not isolated, but instead reacted directly with the salt of the general formula (4) or (5). The reactants are preferably employed in approximately equimolar amount, with, on use of the acylbis(trifluoromethyl)amide, this being employed in twice the equimolar amount.

If the salt of the general formula (4) or (5) is employed in the form of its fluoride, i.e. if $\text{E}^- = \text{F}^-$, the reaction according to the invention can be carried out directly in a one-pot reaction and without added alkali metal fluoride DF.

It is possible for volatile by-products to form, which are then removed under reduced pressure. Usually, however, by-products form which are insoluble in the solvents used and are separated off by filtration. The solvent is, if desired, removed together with volatile by-products under reduced pressure. The salts according to the invention can generally be isolated with yields above 80%.

In order to improve the purity if too low, the salt according to the invention can be dissolved in a polar organic solvent and treated with rubidium imide $\text{Rb}^+ \text{N}(\text{CF}_3)_2^-$. The precipitating rubidium salt which forms is then filtered off, and the solvent is removed under reduced pressure.

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The alkali metal fluoride used in accordance with the invention is preferably potassium or rubidium fluoride, particularly preferably the less expensive potassium fluoride.

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The polar organic solvent which is preferred in accordance with the invention is selected from the group acetonitrile, dimethoxyethane, dimethylformamide and propionitrile.

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The reaction according to the invention is preferably carried out at temperatures between -40°C and 80°C , in particular between 0°C and 40°C and very particularly preferably at room temperature.

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All compounds according to the invention have a salt-like character, relatively low melting points (usually below 100°C) and can be used as ionic liquids.

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The salts according to the invention can be employed as solvents for many synthetic or catalytic reactions, for example Friedel-Crafts acylation and alkylation, Diels-Alder cycloadditions, hydrogenation and oxidation reactions, Heck reactions. Furthermore, fluorinated solvents, for example, can be synthesised for secondary and primary batteries.

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They are suitable as reagents for the introduction of $\text{N}(\text{CF}_3)_2$ groups. For example, $\text{N}(\text{CF}_3)_2$ groups can substitute the halogen atoms in organic halogen compounds. Furthermore, the salts according to the invention are of interest as precursors for the preparation of liquid-crystal compounds and of active ingredients, inter alia, for medicaments and crop-protection agents.

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The use of the compounds according to the invention as non-aqueous electrolyte, if desired in combination with other electrolytes known to the person skilled in the art, is also possible.

In addition, the salts according to the invention can be used as non-aqueous, polar substances in suitable reactions as phase-transfer catalyst or as medium for the heterogenisation of homogeneous catalysts.

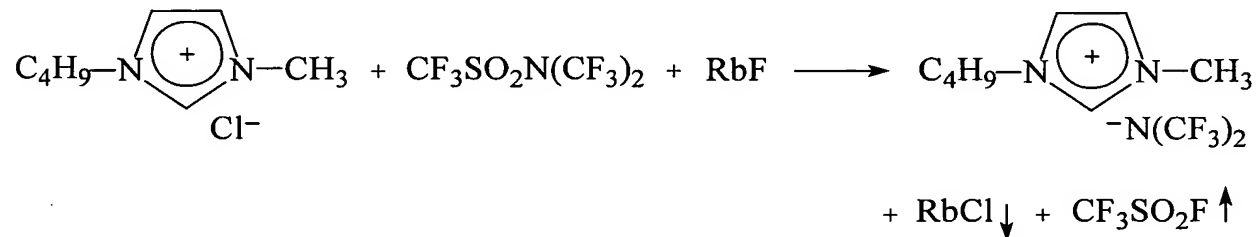
- 5 The complete disclosure content of all applications, patents and publications mentioned above and below is incorporated into this application by way of reference.

Even without further comments, it is assumed that a person skilled in the art will be able to utilise the above description in the broadest scope. The preferred embodi-
 10 ments and examples should therefore merely be regarded as descriptive disclosure which is absolutely not limiting in any way.

All NMR spectra were measured on a Bruker Avance 300 spectrometer (^1H : 300.13 MHz, ^{19}F : 282.40 MHz).

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Example 1



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A solution of 2.93 g (12.3 mmol) of $\text{Rb}^+ \text{N}(\text{CF}_3)_2^-$, which was prepared from 1.29 g (12.3 mmol) of RbF and 3.63 g (12.7 mmol) of $\text{CF}_3\text{SO}_2\text{N}(\text{CF}_3)_2$ in 10 cm³ of dry acetonitrile, is added at room temperature with stirring to a solution of 2.15 g (12.3 mmol) of 1-butyl-3-methylimidazolium chloride in 5 cm³ of dry acetonitrile.

- 25 The reaction mixture is stirred at room temperature for 15 min, and the precipitating RbCl is filtered off and washed with dry acetonitrile (2 x 5 cm³). The acetonitrile is removed under a vacuum of 120 Pa, and the residue is dried for 2 hours at 50°C under reduced pressure, giving 3.24 g of oil-like substances.

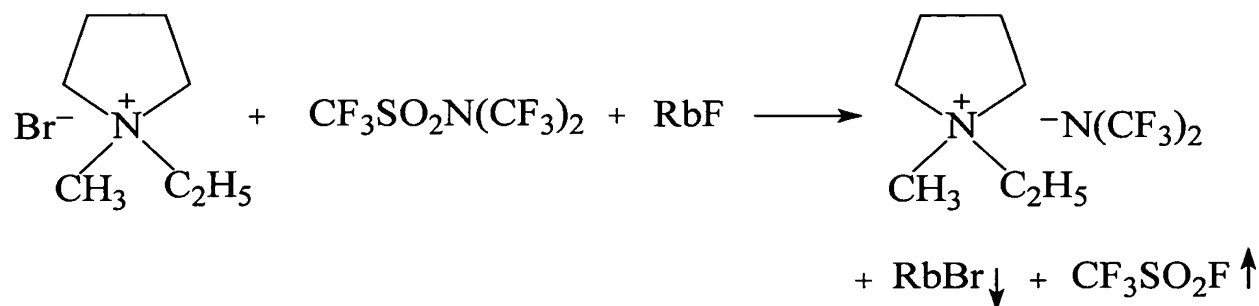
- 30 The yield of 1-butyl-3-methylimidazolium bis(trifluoromethyl)imide, $[\text{C}_8\text{H}_{15}\text{N}_2]^+ \text{N}(\text{CF}_3)_2^-$, is 90.5%.

^{19}F -NMR (reference: CCl_3F ; solvent: CD_3CN): -37.35 s

^1H -NMR (reference: TMS ; solvent: CD_3CN): 0.93 t (CH_3); 1.32 m (CH_2); 1.83 m (CH_2); 3.87 s (CH_3); 4.17 t (CH_2); 7.46 dd (CH); 7.51 dd (CH); 9.08 br s (CH); $J^3_{\text{H,H}} = 7.3 \text{ Hz}$; $J^3_{\text{H,H}} = 7.4 \text{ Hz}$; $J_{\text{H,H}} = 1.8 \text{ Hz}$

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Example 2



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A solution of 4.65 g (19.6 mmol) of $\text{Rb}^+ \text{N}(\text{CF}_3)_2^-$, which was prepared from 2.05 g (19.6 mmol) of RbF and 5.95 g (20.9 mmol) of $\text{CF}_3\text{SO}_2\text{N}(\text{CF}_3)_2$ in 20 cm^3 of dry acetonitrile, is added at room temperature with stirring to a solution of 3.65 g (18.8 mmol) of N-methyl-N-ethylpyrrolidinium bromide in 20 cm^3 of dry acetonitrile.

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The reaction mixture is stirred at room temperature for 15 min, and the precipitating RbBr is filtered off and washed with dry acetonitrile ($2 \times 5 \text{ cm}^3$). The acetonitrile is removed under a vacuum of 1.4 Pa, and the residue is dried for 2 hours at $60\text{--}65^\circ\text{C}$ under reduced pressure, giving 4.68 g of solid substances. The melting point is $80\text{--}85^\circ\text{C}$.

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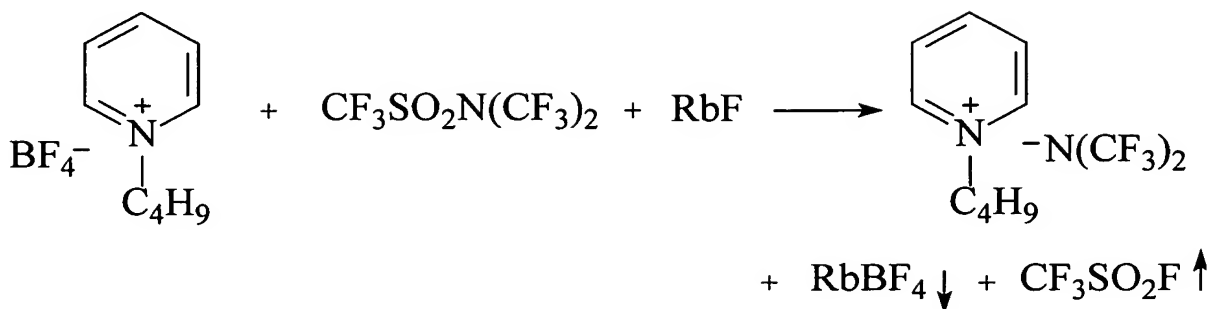
The yield of N-methyl-N-ethylpyrrolidinium bis(trifluoromethyl)imide, $[\text{C}_7\text{H}_{16}\text{N}]^+ \text{N}(\text{CF}_3)_2^-$, is 93.4%.

^{19}F -NMR (reference: CCl_3F ; solvent: CD_3CN): -36.36 s

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^1H -NMR (reference: TMS ; solvent: CD_3CN): 1.34 tm (CH_3); 2.17 m (2CH_2); 2.27 s (CH_3); 3.38 q (CH_2); 3.47 m (2CH_2); $J^3_{\text{H,H}} = 7.3 \text{ Hz}$

Example 3



- 5 A solution of 6.93 g (29.2 mmol) of $\text{Rb}^+ \text{N}(\text{CF}_3)_2^-$, which was prepared from 2.05 g (29.2 mmol) of RbF and 8.43 g (29.6 mmol) of $\text{CF}_3\text{SO}_2\text{N}(\text{CF}_3)_2$ in 20 cm³ of dry acetonitrile, is added at room temperature with stirring to a solution of 6.50 g (29.1 mmol) of N-butylpyridinium tetrafluoroborate in 15 cm³ of dry acetonitrile. The reaction mixture is stirred at room temperature for 15 min, and the precipitating RbBF₄ is filtered off and washed with dry acetonitrile (2 x 5 cm³). The acetonitrile is removed under a vacuum of 1.4 Pa, and the residue is dried for 2 hours at
- 10 60-65°C under reduced pressure, giving 8.28 g of oil-like substances.

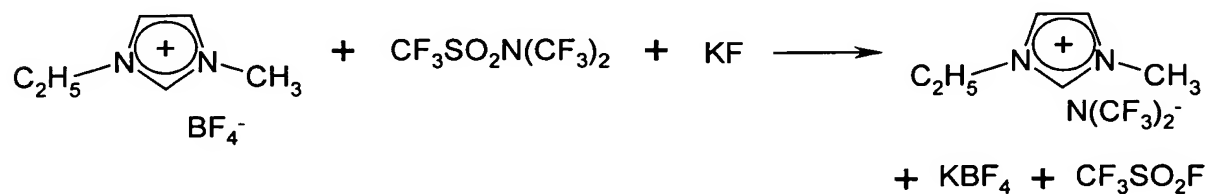
- 15 The yield of N-butylpyridinium bis(trifluoromethyl)imide, $[\text{C}_9\text{H}_{14}\text{N}]^+ \text{N}(\text{CF}_3)_2^-$, is 98.7%.

¹⁹F-NMR (reference: CCl₃F; solvent: CD₃CN): -36.23 s

- 20 ¹H-NMR (reference: TMS ; solvent: CD₃CN): 0.95 t (CH₃); 1.38 m (CH₂); 1.96 m (CH₂); 4.59 t (CH₂); 8.06 m (2CH); 8.54 tt (CH); 8.92 dm (2CH); J³_{H,H} = 7.3 Hz; J³_{H,H} = 7.5 Hz; J_{H,H} = 7.9 Hz; J_{H,H} = 1.3 Hz

Example 4

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A solution of $K^+ N(CF_3)_2^-$, which was prepared from 1.90 g (32.7 mmol) of spray-dried potassium fluoride KF and 9.14 g (32.1 mmol) of $CF_3SO_2N(CF_3)_2$ in 25 cm³ of dry dimethylformamide, is added at room temperature with stirring to a solution of 6.28 g (31.7 mmol) of 1-ethyl-3-methylimidazolium tetrafluoroborate in 10 cm³ of dry dimethylformamide. The reaction mixture is stirred at room temperature for 15 min and subsequently cooled using an ice bath. The precipitating KBF_4 is filtered off and washed with dry dimethylformamide (10 cm³). The solvent is removed at 30-35°C under a vacuum of 1.3 Pa. The liquid is separated from the precipitate, giving 7.8 g of red-yellowish, oil-like substances.

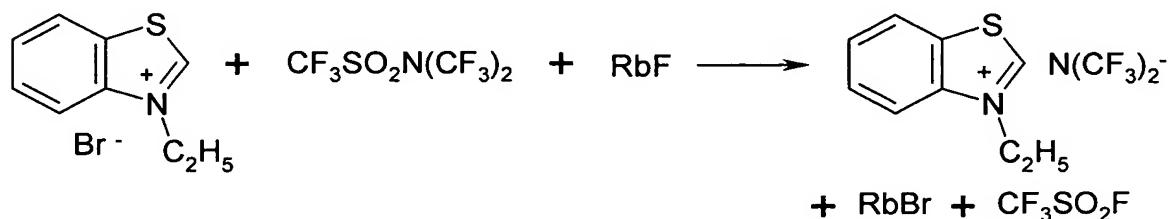
The yield of 1-ethyl-3-methylimidazolium bis(trifluoromethyl)imide, $[C_6H_{11}N_2]^+ N(CF_3)_2^-$, is 93.5% with a purity (according to ¹⁹F-NMR measurement) of 86.5%.

In order to improve the purity, the salt is dissolved in 10 cm³ of dry acetonitrile and treated with a solution of 1.35 g (5.7 mmol) of $Rb^+ N(CF_3)_2^-$ in 8 cm³ of dry acetonitrile at room temperature. The precipitating $RbBF_4$ is filtered off and washed with dry acetonitrile (5 cm³). The acetonitrile is removed at 30-35°C under a vacuum of 1.3 Pa, giving 7.8 g of 1-ethyl-3-methylimidazolium bis(trifluoromethyl)imide, $[C_6H_{11}N_2]^+ N(CF_3)_2^-$, having a purity of 98%.

¹⁹F-NMR (reference: CCl_3F ; solvent: CD_3CN): -36.41 s

¹H-NMR (reference: TMS ; solvent: CD_3CN): 1.45 t (CH_3); 3.84 s (CH_3); 4.18 q (CH_2); 7.40 t (CH); 7.46 t (CH); 8.92 br. s (CH); $J^3_{H,H} = 7.3$ Hz; $J_{H,H} = 1.8$ Hz

Example 5



A solution of 0.69 g (2.9 mmol) of $Rb^+ N(CF_3)_2^-$, which was prepared from 0.303 g (2.9 mmol) of rubidium fluoride RbF and 0.83 g (2.9 mmol) of $CF_3SO_2N(CF_3)_2$ in 5 cm³ of dry acetonitrile, is added at -35 to -38°C with stirring to a solution of

0.71 g (2.9 mmol) of N-ethylbenzothiazolium bromide in 10 cm³ of dry acetonitrile. The reaction mixture is stirred at -35 to -38°C for 15 min, and the precipitated RbBr is subsequently filtered off at this temperature and washed with dry acetonitrile (2 x 5 cm³). The residue are 0.48 g of rubidium bromide (positive sample with silver nitrate and no signals in the ¹H and ¹⁹F NMR spectra). NMR-spectroscopic investigation of the acetonitrile solution at low temperature (-30°C) showed the formation of N-ethylbenzothiazolium bis(trifluoromethyl)imide.

¹⁹F-NMR (reference: CCl₃F; solvent: CD₃CN): -39.15 s